

Materials Research Outreach Program Symposium

February 1st and 2nd

2017

MRL

Materials Research Laboratory at UCSB: An NSF MRSEC
UNIVERSITY OF CALIFORNIA, SANTA BARBARA



Cover Figures

Left: Poster 10

Examining the Impact of Dispersity on Polymeric Materials

J. Lawrence, B. Oschmann, J. M. Ren, D-S. Kim, S-H. Lee, A.S. Knight, E. Goto, C. Zhang, A. Abdilla, M. Nothling, A. Abrams, A. Levi, C. Bates, L. Connal, P. G. Clark, C. J. Hawker

Discrete oligo(3-hexylthiophene) samples (4-mer to 12-mer), isolated from one synthesis-purification step.

Middle: Poster 32

Thermoelectric Properties of Half-Heusler Materials: Role of Microstructure and Disorder

M. Buffon, E. Levin, J. Douglas, S. Mooraj, T. Pollock, R. Seshadri

TEM micrograph highlighting the interface formed between half-Heusler NbCoSn (matrix) and Heusler NbCo₂Sn (particulates).

Right: Poster 34

Transport in Complex Oxides: Understanding Mobility from First Principles

W. Wang, M. Swift, K. Krishnaswamy, Y. Kang, B. Himmetoglu, C. G. Van de Walle

Illustration of electron-phonon scattering in a complex oxide.

**Materials Research Outreach Symposium
February 1 & 2, 2017, Corwin Pavilion, University Center**

Daniel Gianola, Symposium Host

Session 1, Wednesday Morning, February 1, 2017, Corwin Pavilion

Session Chair: Daniel Gianola

8:15 am	<i>Breakfast</i>	
8:45 am	<i>Opening remarks by the Deans</i>	
9:00 am	Mahdi Abu-Omar, UCSB	Renewable Thermosets Derived from Lignin
9:30 am	Vicky Doan-Nguyen, UCSB	Bridging Form and Function: A Structural Investigation of Chalcogels as Li-Ion Battery Electrodes
10:00 am	<i>Refreshment Break</i>	
10:30 am	Eoghan Dillon, Anasys Instruments	Recent Advances in Nanoscale Infrared Spectroscopy
11:00 am	Karthik Krishnaswamy, UCSB	Modeling Electron Transport from First Principles
11:30 am	Kunal Mukherjee, UCSB	Lattice Mismatched Epitaxy and Microstructural Characterization of Compound Semiconductors for Optoelectronic Devices
12:00 pm	<i>Lunch</i>	

Session 2, Wednesday Afternoon, February 1, 2017, Corwin Pavilion

Session Chair: Craig Hawker

1:30 pm	Renee Rottner, UCSB	Weeding Out the Competition: How Alternatives are Eliminated During Institutionalization
2:00 pm	Chris Bates, UCSB	Patterning With Block Copolymers: Recent Advances in High-Resolution Lithography
2:30 pm	<i>Refreshment Break</i>	
3:00 pm	Gabriel Sanoja, UCSB	Molecular Engineering of Polymerized Ionic Liquids
3:30 pm	Cheetham Lecture: Professor Jennifer Lewis, Harvard University	Digital Assembly of Architected Materials
4:30 pm	<i>Posters and Reception</i>	

**Materials Research Outreach Symposium
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Daniel Gianola, Symposium Host

Session 3, Thursday Morning, February 2, 2017, Corwin Pavilion

Session Chair: Rachel Segalman

8:30 am	<i>Breakfast</i>	
9:00 am	Bert Meijer , TU Eindhoven	Functional Supramolecular Systems and Materials
9:30 am	Emily Wonder , UCSB	Decorating Cationic Liposome-Nucleic Acid Nanoparticles for Gene Delivery
10:00 am	<i>Refreshment Break</i>	
10:30 am	John Sarrao , LANL	Mesoscale Science: Science Frontier and Technology Opportunity
11:00 am	Michelle Johannes , NRL	Making Li-Ion Battery Materials Better and Safer
11:30 am	Sam Daly , UCSB	Linking Length Scales: The Effect of the Microscale on Material Failure
12:00 pm	<i>Lunch</i>	

Session 4, Thursday Afternoon, February 2, 2017, Corwin Pavilion

Session Chair: Ram Seshadri

1:30 pm	Lynne Walker , Carnegie	Impact of Dispersed Particles on the Structure and Flow Mechanism of Block Copolymer Micelle Solutions and Soft Solids
2:00 pm	Athina Anastasaki , UCSB	Atom Transfer Radical Polymerization (ATRP) for Everyone; Simplifying Traditional ATRP to Afford Well-Defined Polymers
2:30 pm	Amalie Frischknecht , Sandia	Simulation of Morphology and Dynamics in Ion-Containing Polymers
3:00 pm	<i>Refreshment Break</i>	
3:30 pm	Bob Lansdorp , Milo Sensors	The Skin is a Superhighway of Small Molecules
4:00 pm	Vincent Gambin , Northrup-Grumman	Materials Research in RF Microelectronics for Aerospace Applications
4:30 pm	Irene Beyerlein , UCSB	Defects and Interfaces in Structural Composites
5:00 pm	<i>Posters and Reception</i>	

About the MROP

Initiated in 1999 under the leadership of Professor Ed Kramer to annually showcase MRL research to our industrial and venture partners, the Materials Research Outreach Program has evolved into so much more. In addition to providing a wonderful opportunity to interface with our corporate colleagues — including local start-ups — the MROP has emerged as the principal occasion to hear about and share UCSB research in the broad Materials arena.

The MROP has traditionally encouraged many newly-joined faculty members from a cross-section of UCSB Departments to showcase their research vision, leading to the nucleation of numerous collaborations. Key academic scientists, particularly from neighboring campuses are also invited. Finally, the MROP has become an integral part of the undergraduate and graduate education, and post-doctoral experience of literally hundreds of students and fellows from Science and Engineering Departments on this campus.

No matter which category best fits you, please feel welcome to attend the 2017 MROP, and thank you for your continued support. We hope you enjoy the MROP as much as we enjoy organizing it.

Materials Research Outreach Symposium
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MROP 2017 Speaker

Dr. Mahdi M. Abu-Omar completed his Ph.D. from Iowa State University and postdoc from Caltech with Harry Gray. He is the Mellichamp Professor of Green Chemistry in the Department of Chemistry and Biochemistry at the University of California, Santa Barbara (UCSB), and the associate director of the Center for Catalytic Conversion of Biomass to Biofuels (C₃Bio), an Energy Frontiers Research Center funded by the Department of Energy. Mahdi is the Founder and President of Spero Energy, Inc., a green specialty chemicals company and a technology provider for the manufacture of high value renewable chemicals from biomass. He has published more than 130 original research papers in peer-reviewed journals. His research interest is in the areas of sustainability and green chemistry through the development and understanding of inorganic catalysts. He is a Fellow of the American Association for Advancement of Science (AAAS) since 2012 and was a Senior Fulbright Fellow (2008). His recognitions include the Crano Memorial Lectureship from ACS Akron Section (2013), JPP Young Investigator Award from the Society of Porphyrins and Phthalocyanines (2010), Beckman Young Investigator Award (1999), and NSF CAREER Award (1998). He chaired the Gordon Research Conference on Inorganic Reaction Mechanisms in 2013.

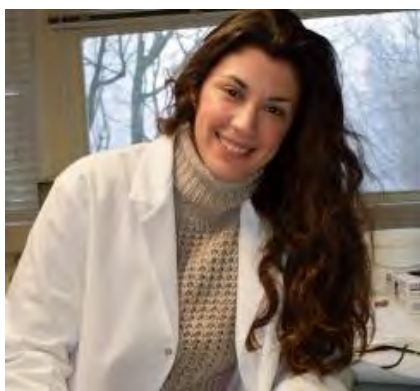


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Dr. Athina Anastasaki graduated from the University of Athens in 2011 with 1st class Honours. She then undertook a Ph.D. in Polymer Chemistry at the University of Warwick under the supervision of Professor David Haddleton, sponsored by Lubrizol. In September 2014 she successfully defended her Ph.D. thesis entitled “Shining a Light on Copper Mediated Living Radical Polymerization: Maximizing End-group Fidelity”. During her candidature she also spend a 2 month period at the University of Pennsylvania (USA), where she worked on single electron transfer living radical polymerization (SET-LRP) methods under the direction of the inventor of this technique (Professor Virgil Percec). Alongside her industrial PhD project she took the initiative to investigate multiple areas of academic interest including sequence-controlled polymers, photochemistry, mechanistic studies, glycochemistry and polymer/protein conjugates. As recognition of her significant developments she was awarded (by the Royal Society of Chemistry) the Jon Weaver prize (2015) for the best PhD in polymer science in UK and she was invited to deliver a prize lecture. In addition, she has been the recipient of multiple awards including the award for the best PhD in Chemistry at the University of Warwick (2015), the award for the top 10 reviewers in Polymer Chemistry for significant contribution to the journal (2016) as well as several travel and conference awards. Following her PhD she commenced a short research fellow position which allowed her to work simultaneously in two research groups (Australia/Davis and UK/Haddleton), where she developed novel sulfur and copper free sequence-controlled materials and thermoresponsive nanoaggregates with tuneable morphologies. She is the author of >50 peer reviewed publications and book chapters and her work has been cited in excess of 1300 times. Currently she is a Global Marie Curie fellow and an Elings fellow working alongside Professor Craig Hawker at UCSB focusing on bio mimicking nanostructure materials and functional polymeric architectures with unique phase separation behaviour.



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Christopher M. Bates earned a B.S. degree in Chemistry at the University of Wisconsin–Madison in 2007 and received a Ph.D. from The University of Texas at Austin in 2013 under the guidance of C. Grant Willson. After a postdoc with Robert H. Grubbs at the California Institute of Technology, Christopher recently moved to the University of California, Santa Barbara as an Assistant Professor in the Materials and Chemical Engineering Departments.



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Irene J. Beyerlein received her Ph.D. degree in Theoretical and Applied Mechanics at Cornell University in March 1997. In July 1997 and for the following three years, she was a J. R. Oppenheimer Fellow at Los Alamos National Laboratory (LANL). Afterwards, she remained on the scientific staff in the Materials Science Division and later, Theoretical Division, until June 2016. Currently, she is a Professor at the University of California at Santa Barbara with a joint appointment in the Mechanical Engineering Department and Materials Department. She has over 250 peer-reviewed publications, five book chapters on subjects ranging from atomistic to continuum scale modeling of advanced materials, two review articles in *Progress in Materials Science*, and a book co-authored with V. M. Segal, entitled, "Fundamentals and Engineering of Severe Plastic Deformation". She is an Editor for *Acta Materialia* and *Scripta Materialia* and Associate Editor for the *Journal of Engineering Materials and Technology*.



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MROP 2017 Speaker

Samantha Daly is an Associate Professor in the Department of Mechanical Engineering at the University of California at Santa Barbara. She received her Ph.D. and M.S. degrees in the Division of Engineering and Applied Science at Caltech in 2007 and 2002 respectively, and subsequently joined the faculty at the University of Michigan, where she was on the faculty until 2016 prior to her move to UCSB. Her interests lie at the intersection of experimental mechanics and materials science, with an emphasis on using novel methods of experimentation coupled closely with theoretical and computational modeling. Group research focuses on the statistical quantification of microstructural features of materials and their effect on meso- and macro-scale properties. Currently, the group is engaged in the development of novel methods of multi-scale material characterization, with application to active materials, high temperature ceramics, very high cycle and low cycle fatigue mechanisms, plasticity, fracture, and material behavior at the microscale. Her recognitions include the NSF CAREER Award, the ASME Eshelby Mechanics Award, the Journal of Strain Analysis Young Investigator Award, the *Experimental Mechanics* Best Paper of the Year Award, the *IJSS* Best Paper of the Year Award, the DOE Early Career Award, the AFOSR-YIP Award, the ASME Orr Award, the Caddell Award, and a number of teaching recognitions.



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Growing up in Dublin, **Eoghan Dillon** received his undergraduate degree in physics and physics technology at Dublin Institute of Technology, Kevin Street in 2005. He was awarded a place on the FAS Science Challenge program which placed him on a six month internship at Rice University in Houston, Texas. Staying at Rice University after the internship he earned his PhD in Chemistry in 2012, with research focused on the efficient capture of CO₂ using polyethyleneimine functionalized nanocarbons. During this time he published multiple scientific papers in peer reviewed journals. He has spoken at most of the major conferences in the U.S. including ACS, MRS, AVS, ISPAC and BPS. Eoghan is currently an applications scientist at Anasys Instruments, a nanoscale analysis company based in Santa Barbara, California. There he specializes in AFM based techniques such as nanoscale infrared spectroscopy and nanoscale thermal analysis.



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Vicky Doan-Nguyen is University of California President's Postdoctoral Fellow and Elings Prize Fellow at the California NanoSystems Institute and the Materials Research Laboratory at the University of California, Santa Barbara. Her research includes synthesis, operando structural characterization, and functional testing of advanced materials for energy storage and conversion. Vicky earned a B.S. in Chemistry and Women's and Gender Studies from Yale University and an M.S. and a Ph.D. in Materials Science and Engineering from the University of Pennsylvania. She has been recognized by the American Crystallographic Association for her work in powder diffraction.



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Amalie L. Frischknecht received her BA in physics and mathematics from Pomona College in 1992 and her PhD in physics from the University of California, Santa Barbara in 1998. She did postdocs at ExxonMobil Research and Engineering (1998-2000) and at Sandia National Laboratories (2000-2003), before becoming a member of technical staff at Sandia in 2003. Dr. Frischknecht is currently a Principal Member of Technical Staff at Sandia National Laboratories, and a staff scientist at the Center for Integrated Nanotechnologies, a DOE Nanoscale Science Research Center and user facility at Sandia and Los Alamos National Labs. She is a Fellow of the American Physical Society. Her research interests are in the statistical mechanics and molecular simulation of complex fluids, including polymer nanocomposites, ion-containing polymers, and charged soft matter systems.



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Vincent Gambin received his PhD from Stanford University in Material Science and Engineering. He is currently leading the New Semiconductors and Devices group in NG Next Basic Research studying new materials and devices for next generation electronics. He is also the principal investigator for DARPA's ICECool Applications program developing high-power GaN MMICs cooled with embedded diamond microfluidics. He's worked at Northrop Grumman for 15 years in the field of high-speed RF electronics developing advanced GaAs, InP and GaN devices.



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Michelle Johannes received her Ph.D in computational physics in 2003 from the University of California at Davis. She spent 1.5 years as a National Research Council postdoctoral fellow at the Naval Research Laboratory (NRL) where she subsequently took a position as a Research Physicist. She currently serves as Section Head of the Center for Computational Material Science at NRL where she continues her computational work on Li-ion battery materials, magnetism, superconductivity, and nanoscale transport. She has won the NRL Berman Award for best publication five times and was named the Sigma Xi Young Researcher in 2011. She became a fellow of the American Physical Society in 2012.



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Karthik Krishnaswamy received his Bachelor of Engineering degree from the M. S. Ramaiah Institute of Technology (MSRIT) in Bangalore in 2011, and his Master of Science degree from the University of California, Santa Barbara in 2013. The primary focus of his research work is employing ab-initio techniques combined with device-level simulations to gain fundamental insights into the properties of novel electronic materials. His research interests are oriented towards creating useful electronic applications based on novel materials in the field of low-power electronics, solid-state lighting, and energy harvesting.



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Bob Lansdorp joined the Saleh Lab at UCSB in 2011 to develop single-molecule instruments for the study of fundamental biophysics. While pursuing his PhD, Bob joined team Milo, one of approximately forty teams entering the 2015 UCSB New Venture Competition. Milo won the competition with a concept for a wearable alcohol sensor and within six months Bob successfully defended his PhD and co-founded Milo Sensors, Inc. The newly-formed company won \$100,000 in the NIH/NIAAA Wearable Alcohol Biosensor Challenge, moved into the CNSI Incubator Laboratory, and raised a Seed Investment Round. At the 2017 Consumer Electronics Show, Milo Sensors unveiled PROOF™: the first wearable for alcohol. Bob currently serves as CTO of Milo Sensors, and is interested in seeing PROOF™ reach the market, but also in learning how future generations of transdermal sensors could lead to improved medical diagnostics.



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Jennifer A. Lewis joined the faculty of the School of Engineering and Applied Sciences and the Wyss Institute for Biologically Inspired Engineering at Harvard University in 2013. Prior to joining Harvard, she was a professor and served as Director of the Materials Research Laboratory at University of Illinois. She has received numerous awards, including the NSF Presidential Faculty Fellow Award, the Langmuir Lecture Award from the American Chemical Society, and the MRS Medal Award. She is a Fellow of the National Academy of Inventors, the American Academy of Arts and Sciences, the American Ceramic Society, the American Physical Society, and the Materials Research Society. Her work on microscale 3D printing was highlighted as one of the “10 Breakthrough Technologies” by the *MIT Technology Review*, while her bioprinting research was named “one of the top 100 science stories” by *Discover Magazine*. She is a co-founder of two companies that are commercializing technology from her lab.

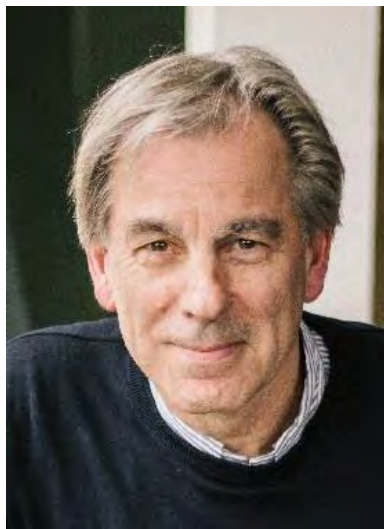


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E.W. “Bert” Meijer is Distinguished University Professor in the Molecular Sciences, Professor of Organic Chemistry at the Eindhoven University of Technology and scientific director of the Institute for Complex Molecular Systems. After receiving his PhD degree at the University of Groningen with Hans Wynberg, he worked for 10 years in industry (Philips and DSM). In 1991 he was appointed in Eindhoven, while in the meantime he has held part-time positions in Nijmegen and Santa Barbara, CA. Bert Meijer is a member of many editorial advisory boards, including *Advanced Materials*, *Angewandte Chemie*, and the *Journal of the American Chemical Society*. Bert Meijer has received a number of awards, including the Spinoza Award in 2001, the ACS Award for Polymer Chemistry in 2006, the AkzoNobel Science Award 2010, the International Award of the Society of Polymer Science Japan in 2011, the Cope Scholar Award of the ACS in 2012, and the Prelog medal in 2014. He is a member of a number of academies and societies, including the Royal Netherlands Academy of Science, where he is appointed to Academy Professor in 2014.



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Kunal Mukherjee received the B.Eng. (Hons.) degree in electrical engineering from Nanyang Technological University, Singapore, in 2007 and the Ph.D. degree in materials science and engineering from the Massachusetts Institute of Technology, Cambridge, MA, USA, in 2014. He was a transceiver engineer at Finisar Corporation in 2009-10, and has been a postdoctoral researcher at MIT and IBM T.J. Watson research center in 2015 and 2016 respectively. He is currently an Assistant Professor in the Materials Department at the University of California Santa Barbara.



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Renee Rottner is an Assistant Professor of Technology Management at UC Santa Barbara, and previously on the faculty at New York University's Stern School of Business. Her research and teaching focuses on innovation, particularly how innovators can improve the development of new ideas and new firms. She has examined the dynamics of innovation in a range of settings, including Caltech spinouts, NASA projects, semiconductor startups, and Federal nanotechnology initiatives. She is currently studying these dynamics in non-US contexts, including entrepreneurship in Japan and China. Before entering academia, Dr. Rottner worked as an entrepreneur, helping engineers and scientists to commercialize their ideas in a variety of contexts including the military, R&D institutes, and universities. She received her B.S. from Eastern Michigan University, her M.S. in Management Science and Engineering from Stanford University, and her Ph.D. in Management from UC Irvine.



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Gabriel E. Sanoja (Gabo) earned his B.S in Course 10 (Chemical Engineering) from MIT in June 2012. His undergraduate research with Prof. Bradley D. Olsen focused on understanding the nature of protein interactions governing the self-assembly of globular protein-polymer block copolymer for development of novel biomaterials with applications in energy conversion and medical therapeutics. He also performed research on bioinorganic chemistry with Prof. Stephen J. Lippard at MIT, and polymer-nanoparticle composites with Prof. Rachel A. Segalman at UC Berkeley.

Gabo moved to UC Berkeley for his graduate studies, where he earned a Ph.D. in Chemical Engineering on December of 2016. He was a student of Prof. Rachel A. Segalman and closely advised by Prof. Nathaniel A. Lynd as part of the Joint Center for Artificial Photosynthesis. Together with Prof. Segalman, Gabo moved to UC Santa Barbara in August 2015 to finish his Ph.D. His research focused on developing a molecular engineering strategy for ion-containing polymers that allows for fine and independent control over polymer properties including the chain length, fraction and chemistry of ionic moieties, and architecture. This strategy opened new avenues to address fundamental questions of polymer science, as well as to enable generation of high-performance functional materials.

After finishing his Ph.D., Gabo became a post-doctoral scholar at the Institute for Collaborative Biotechnologies of UC Santa Barbara. He is currently using state-of-the-art polymer and organic chemistry to determine the upper limits of thermoelectric performance of ion-containing polymers.



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John Sarrao is the Associate Director for Theory, Simulation, and Computation (AD-TSC) at Los Alamos National Laboratory (LANL). As AD-TSC, he leads the Laboratory's efforts in applying science-based prediction to existing and emerging national security missions. TSC is a ~700 person organization spanning the Laboratory's Theoretical; Computer, Computational, and Statistical Sciences; and High Performance Computing organizations. Previously, Sarrao was the Program Director for Los Alamos National Laboratory's Office of Science Programs and for MaRIE (Matter-Radiation Interactions in Extremes), LANL's signature facility concept which will provide transformational materials solutions for national security challenges. John has also served on a number of U.S. Department of Energy Basic Energy Sciences Advisory Committee (BESAC) Subcommittees, helping to set strategic directions for materials research.

John's primary research interest is in the synthesis and characterization of correlated electron systems, especially actinide materials. He was the 2013 winner of the Department of Energy's E.O. Lawrence Award and the 2004 winner of the LANL Fellows Prize for Research, in part for his discovery of the first plutonium superconductor. He is a Fellow of the American Association for the Advancement of Science (AAAS), the American Physical Society (APS), and Los Alamos National Laboratory. John received his Ph.D. in physics from the University of California, Los Angeles based on thesis work performed at LANL.



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MROP 2017 Speaker

Lynn M. Walker is a Professor of Chemical Engineering and both Chemistry (by courtesy) and Materials Science & Engineering (by courtesy) at Carnegie Mellon University. She holds a B.S. degree from the University of New Hampshire and a Ph.D. from the University of Delaware, both in chemical engineering. She was an NSF International Postdoctoral Fellow at the Katholieke Universiteit in Leuven, Belgium before joining Carnegie Mellon University in 1997. She spent 2007 as a visiting professor at the Polymer IRC at the University of Leeds in the United Kingdom. Her research focuses on quantifying the coupling between flow behavior and flow-induced microstructure in complex fluids. Current research focuses in two directions; quantifying the influence of flow on self-assembled nanostructures and controlling transport to complex fluid-fluid interfaces. She is the recipient of the DuPont Young Faculty Research Grant and an NSF CAREER award. She has twice been recognized for teaching by receiving the Kun Li Award for Excellence in Education from the Department of Chemical Engineering at Carnegie Mellon University, is the 2016 recipient of the Lazarus Award for Mentoring from CMU and the 2015 WIC Mentorship Excellence Award from AIChE. She is the Editor-in-Chief of *Rheologica Acta* and serves on the editorial boards of the *Journal of Rheology* and *Industrial & Engineering Chemistry Research*. She is a member of the E&PS technical advisory board at Dow Chemical, as well as serving on committees for AIChE and the Society of Rheology. CMU faculty website: <http://www.cmu.edu/cheme/people/faculty/lynn-walker.html>



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Emily Wonder designs and evaluates liposomal gene delivery vehicles as a PhD candidate in the group of Cyrus Safinya. Before joining the Materials Department at UCSB, she studied physics at the University of Chicago.



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- | <u>Poster</u> | <u>Title and Authors</u> |
|---------------|--|
| 1 | Biologically Relevant Cations Remodel Microtubule-Protein Tau Bundles
C. Song, P. Kohl, P. Chung, B. Fletcher, H. Miller, Y. Li, S.C. Feinstein, L. Wilson, C.R. Safinya |
| 2 | Charge Transport in Two-Dimensional Hybrid Halide Compounds
N. Venkatesan, J. Labram, C. Takacs, H. Evans, E. Perry, F. Wudl, M. Chabinye |
| 3 | Coacervates - Preferential Chemical and Physical Reaction Media
R. Mirshafian, K. Ahn, S. Hosseinzadeh, H. L. Viola, P. Zalicki, J. H. Waite |
| 4 | Design and Synthesis of Fullerene Based Metal-Organic Frameworks
G. Betancourt, C. Suarez, L. Echegoyen |
| 5 | Determining Interactions of Cationic Membrane Nanoparticles with Hydrophobic Drug Cargo and Their Mechanisms of Drug Delivery to Cells
V. Steffes, M. Murali, K. Ewert, C. Safinya |
| 6 | Electron-Induced Instability of p-Type Polymer Field-Effect Transistors: Mechanistic Understanding and Mitigating by Fullerenes
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I. Morgan, O. Saleh |
| 8 | Epi-Transfer Technology for UV LEDs Grown on SiC
B. SaifAddin, H. Foronda, A. Almogbel, C. Zollner, M. Iza, S. Nakamura, S. P. DenBaars, J. S. Speck |
| 9 | Evolution of Structural and Electronic Phase Behavior in $Sr_3(Ir_{1-x}Mn_x)_2O_7$
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| 10 | Examining the Impact of Dispersity on Polymeric Materials
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| 11 | Fantastic Magnets and Where to Find Them
J. D. Bocarsly, E. Levin, J. Grebenkemper, T. Pollock, S. Wilson, R. Seshadri |
| 12 | Fe,Ni,N-Containing Mesoporous Carbon Materials as Low-Overpotential Bifunctional Oxygen Reduction and Oxygen Evolution Electrocatalysts
N. P. Zussblatt, D. Kim, V. Boothby, B. F. Chmelka |

- 13 **Hierarchical Structure and Structural Transitions of a Conjugated Polyelectrolyte in Aqueous Solution**
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- 14 **InP Based Lasers and Photodetectors Integrated on Si for Next Generation Data Transmission**
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- 15 ***In situ* Structural Measurements of Soft Materials in Arbitrary Deformation Fields**
P. Corona, N. Ruocco, K. Weigandt, L. G. Leal, M. Helgeson
- 16 **Insulator-Metal Transitions in Complex Palladium Oxides**
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- 17 **Light as a Tool to Reversibly Activate Cross-link Exchange in Vitrimers**
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- 19 **Local Structure Evolution and Corresponding Charge Storage Mechanisms in Transition Metal Sulfides for Lithium Batteries**
M. M. Butala, V. V. T. Doan-Nguyen C. Goebel, S. Arnon, M. A. Lumley, K. Wiadereked, O. Borkiewicz, P. J. Chupas, K. W. Chapman, M. Balasubramanian, R. Seshadri
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P1: Biologically Relevant Cations Remodel Microtubule-Protein Tau Bundles

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Microtubule-associated protein (MAP) Tau, an intrinsically disordered protein, binds to and regulates microtubule dynamics in the axonal compartment in mature neurons. Using synchrotron small-angle X-ray scattering (SAXS) and electron microscopy we recently reported on the discovery that under dissipative out-of-equilibrium conditions (i.e. with added GTP at 37°C), Tau mediates microtubule bundling architectures which mimic microtubule fascicles in the axon initial segment, resulting from aggregate sub- $k_B T$ Tau-mediated attractions. Here we will report on ongoing time-dependent SAXS studies of the response of the reconstituted MT-Tau bundling architectures to the addition of biologically relevant cations under dissipative out-of-equilibrium conditions.

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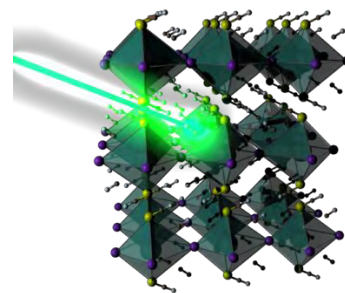
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P2: Charge Transport in Two-Dimensional Hybrid Halide Compounds

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Hybrid-halide perovskite materials have garnered attention because they are earth-abundant, solution processable materials for photovoltaic cells. Two compounds, methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) and formamidinium lead iodide ($\text{CH}(\text{NH}_2)_2\text{PbI}_3$), have primarily been utilized to produce high-efficiency solar cells. Though these two hybrid compounds possess three-dimensional connectivity and attractive electronic properties, however material stability in high moisture and heat remains a major concern. Recently, increased stability has been shown in two-dimensional analogs of the perovskite structure. Two-dimensional layered structures are created by slicing the perovskite structure along certain crystallographic planes. In this study, the two axial iodide atoms in the $\text{CH}_3\text{NH}_3\text{PbI}_3$ structure were replaced with the pseudohalide thiocyanate (SCN^-), creating a layered material. Films with large, well-oriented grains of $(\text{CH}_3\text{NH}_3)_2\text{Pb}(\text{SCN})_2\text{I}_2$ formed during growth by spin coating. X-ray scattering measurements revealed a preferential orientation of sheets layering parallel to the substrate. Optical measurements reveal an absorption band edge of approximately 2 eV with weak emission at lower energy, attributed to triplet excited state. Using time-resolved microwave conductivity (TRMC) experiments, the carrier mobility in-plane was found to be comparable to that of methylammonium lead iodide, with carrier lifetimes on the order of 100 ns. This charge transport data leads us to conclude that a three-dimensional structure is not necessarily a prerequisite for long carrier lifetime and carrier mobility.



Photoexcitation of carriers in $(\text{CH}_3\text{NH}_3)_2\text{Pb}(\text{SCN})_2\text{I}_2$ layered perovskite structure

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P3: Coacervates - Preferential Chemical and Physical Reaction Media

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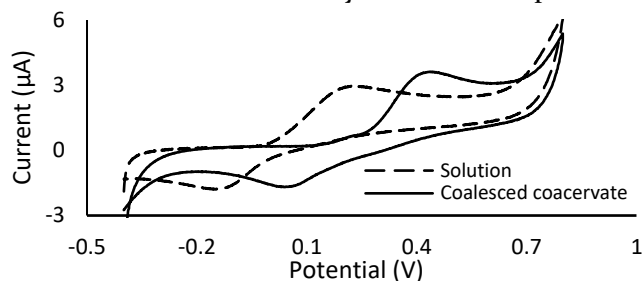
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Polyelectrolyte coacervation, with its greater-than-water density, low interfacial energy, and shear thinning viscosity, mediates the wet adhesion of diverse marine organisms [1,2]. Coacervates have other important properties that are challenging to study due to metastability and a lack of suitable analytical methods. Here, we adapt solution electrochemistry to obtain unprecedented insights about coacervates as reaction media for catechols.

Catechols preferentially partition into coacervated polyelectrolytes with three significant consequences: 1) catechols are concentrated within the coacervate phase, 2) reduced catechol diffusion decreases diffusional loss to the medium, and 3) coacervate-mediated shielding of catechol oxidation enhances control of cohesive and adhesive reactivities of catechol.

Inspired by these insights, a mussel-mimetic adhesive consisting of coacervated polyelectrolytes, low molecular weight catechol and FeCl₃ was formulated for bonding to hydroxyapatite and steel surfaces. Results suggest that, when present in coacervates, low molecular weight catechols can accomplish many of the adhesive properties of catechol-functionalized polymers.



The difference between the oxidation potentials of 5×10^{-5} M 4MC in the coalesced coacervate phase and aqueous phase.

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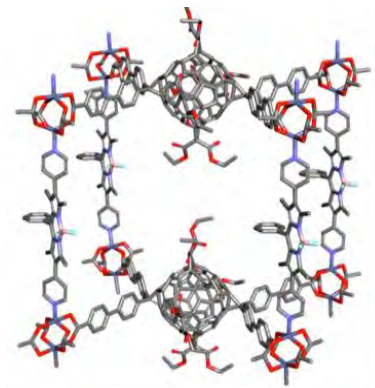
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P4: Design and Synthesis of Fullerene Based Metal-Organic Frameworks

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As the cost of oil and the damage done to the atmosphere increase, new sources of energy have been sought. One of the most promising sources of energy is Hydrogen. This molecule has caught the attention of researchers as it is abundant and the harvest of energy is possible and efficient. In order to use hydrogen gas as a viable source of energy for everyday applications, an effective method for storing this gas has to be developed since current storage methods are impractical and ineffective [1]. Metal Organic Frameworks (MOFs) have shown promising results as hydrogen storage materials. The synthetic flexibility, high stability and hydrogen storage properties of fullerenes make them ideal candidates for their use as linkers in MOFs. Our design was guided by previously reported fullerene-free MOFs that exhibit efficient hydrogen storage capabilities [2]. We report the synthesis of a tetra-COOH fullerene derivative for its use in the construction of fullerene based MOFs for use in hydrogen storage.



Structure of fullerene based MOF

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P5: Determining Interactions of Cationic Membrane Nanoparticles with Hydrophobic Drug Cargo and Their Mechanisms of Drug Delivery to Cells**V. Steffes,^a M. Murali,^a K. Ewert,^a C. Safinya^a**^aUniversity of California, Santa Barbara, CA 93106

Paclitaxel (PTXL), a member of the taxane family of mitotic inhibitors, is a widely used cancer drug. The first PTXL clinical incarnation (Taxol[®]) employs the non-ionic surfactant, Cremophor[®] EL—which itself causes hypersensitivity reactions—to solubilize hydrophobic PTXL. Second generation alternatives to deliver PTXL include Abraxane[®] and EndoTAG[®] (a liposomal formulation), which achieve limited passive tumor targeting and are still associated with typical chemotherapy side effects. In order to make a substantial therapeutic improvement, delivery vehicles must concentrate more PTXL in tumors and interact less with healthy tissue [1–3]. Lipid nanoparticles have many advantages as drug delivery agents including a diverse set of lipid building blocks to tune physical and chemical properties, as well as their ease of modular fabrication. We demonstrate the ability to alter the drug-loading capacity of liposomes and the nanoparticle-cell interactions by changing the lipid composition to affect membrane charge density, steric stabilization, hydrophobic domain disorder, and lipid shape (which determines membrane curvature). Here, we present results that indicate the importance of tail structure for hydrophobic drug loading and retention. We have also observed a non-monotonic drug delivery dependence on the amount of PTXL incorporated into liposomes. Preliminary results reveal a significant divergence from the known tenets governing liposome-based gene delivery to those that determine small molecule hydrophobic drug delivery. In order to develop a set of design principles for the latter, a systematic understanding of how liposome formulation dictates the nanoparticle's subsequent path *in vitro* and *in vivo* is essential. Novel liposome formulations achieve *in vitro* outcomes equal to and better than the stage III formula EndoTAG[®].

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P6: Electron-Induced Instability of p-Type Polymer Field-Effect Transistors: Mechanistic Understanding and Mitigating by Fullerenes

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Operational stability of organic field-effect transistors (OFETs) is a crucial aspect needed to be fully understood for their commercialization. Recently, high hole mobility OFETs have commonly achieved with donor-acceptor (D-A) copolymers, which often exhibit a certain degree of ambipolarity due to the copolymers' low bandgap. It is crucial to know how electron conduction affects the electrical stability of hole conduction in p-type OFETs. In a recent paper, [1] we showed how electron trapping caused the stability of hole current and the double-slope behavior ($I_d^{1/2}$ vs. V_g in transfer curves of saturation regime) of the high-mobility p-type OFETs made from D-A copolymers with SiO₂ dielectrics. The electron trapping and the subsequent formation of -SiO⁻ charges are originated from the interplay of SiO₂ surface and a confined trace amount of water at the interface. It results in considerable positive shift of turn on voltage and the occurrence of double-slope behavior. Recently, the device instability and non-ideality were found to be mitigated by the addition of fullerene derivatives into the polymer solution for device fabrication [2]. We demonstrated that the fullerene acts as an electron acceptor to take electrons that are injected into the polymer. Therefore, electron trapping at the SiO₂ interface is significantly reduced, resulting in the suppression of the device instability and double-slope. More importantly, different electrical measurements were carried out to show that hole transport is not affected by the addition of fullerenes. It can be attributed for the favorable assembly of the polymer on SiO₂ to form the first few nanometers of pure polymer at the interface with the dielectrics, which primarily control the charge transport in OFETs. Our findings provide a new perspective in studying electrical stability of OFETs; and tremendously impact the molecular design and device engineering of OFETs.

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P7: Entropic Elasticity in the Giant Muscle Protein Titin

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Intrinsically disordered proteins (IDPs) are a large and functionally important class of proteins that lack a fixed three-dimensional structure. Instead, they adopt a conformational ensemble of states which facilitates their biological function as molecular linkers, springs, and switches. Due to their conformational flexibility, it can be difficult to study IDPs using typical experimental methods. To overcome this challenge, we use a high-resolution single-molecule magnetic stretching technique to quantify IDP flexibility. We apply this technique to the giant muscle protein titin, measuring its elastic response at low forces. We present results demonstrating that titin's native elastic response derives from the combined entropic elasticity of its ordered and disordered domains.

P8: Epi-Transfer Technology for UV LEDs Grown on SiC

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We present a new epi-transfer technology to enable making high EQE SiC-based AlGaIn Deep UV LEDs, grown by MOCVD. This new technology is based on the removal of the absorbing growth SiC substrate and subsequent epi-transfer of the UV LED structure into a new insulating substrate (See Fig.1a) to make a high extraction thin-film flip-chip (TFFC) UV LED. We present IV and spectra results for thin-film flip-chip (TFFC) at 311 nm with a voltage of 6.9 V at 23 A/cm² (See Fig.1b) with ultrathin p-GaN (10 nm) and with a highly reflective Al based p-contact (pt/Al/Ni,Au). Furthermore, Photoluminescence enhancement measurements demonstrate the potential for increased light extraction from TFFC UV LEDs).

The SiC substrate was removed partly by mechanical grinding, followed by a two-step inductively coupled plasma (ICP) etches: a fast non-selective SF₆ etch; a slow but highly selective SF₆ etch of SiC over AlN to planarize the surface and to stop at a smooth N-AlN surface. At 1000W high ICP power, and 50W substrate bias power the etch selectivity between SiC and AlN was high (>200) with a SiC etch rate of 100 nm/min. Inexpensive fused silica carrier wafers were used to withstand etching of > 100 microns (or more) of SiC, without depleting the plasma's chemistry. Metal-coated carrier wafers were avoided to avoid sputtering metal on the sample or the etching chamber walls. Using a fused silica carrier wafer, etch rates at 1000W ICP coil power is about 0.6 μm per min at a 400W bias and a pressure of 1.33 Pa. The AFM surface roughness of the exposed AlN was ~ 0.6 nm over 25 μm². Exposed N-face AlN surface is roughened with aqueous KOH, which generates hexagonal pyramids that are highly efficient in light extraction. The etching conditions were investigated to optimize light extraction. By varying the etch time and temperature, it was shown that the hexagonal pyramid density is independent of threading dislocations density when etched in aqueous KOH.

This work was supported by the KACST-KAUST- UCSB Solid State Lighting Program (SSLP). Additional support was provided by the Solid State Lighting and Energy Electronics Center (SSLEEC) at UCSB.

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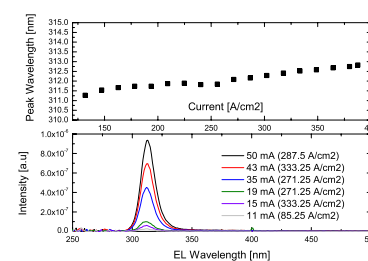
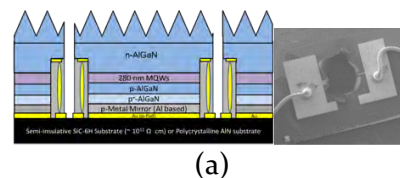


Figure 1: (a) Schematic thin-film flip-chip flip-chip (TFFC) UV LED. (b) EL Spectra from a packaged 310 nm LED with increasing current in mA (the active LED area is 12,900 μm², the FWHM is 20 nm at 387.5 A/cm²)

P9: Evolution of Structural and Electronic Phase Behavior in $\text{Sr}_3(\text{Ir}_{1-x}\text{Mn}_x)_2\text{O}_7$ **J. L. Schmeh, ^a T. Hogan, ^{a,b} W. Tian, ^c S. Wilson^a**^aMaterials Department,
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The Ruddlesden-Popper (RP) iridate $\text{Sr}_3\text{Ir}_2\text{O}_7$ is a rare example of a spin-orbit coupling (SOC) induced $J_{\text{eff}} = 1/2$ Mott antiferromagnet. Its Mott state is extremely sensitive to perturbation introduced by chemical substitution, as is exemplified when hole-doping the B-site with Ru. Here the electronic order is suppressed, leading to a percolative metal-insulator transition. However, strong interplay between localized and itinerant regions stabilizes magnetic ordering well into the metallic phase [1]. Here, we present an investigation of the evolution of the electronic and structural properties of $\text{Sr}_3(\text{Ir}_{1-x}\text{Mn}_x)_2\text{O}_7$, with x up to 44%. Unlike $\text{Sr}_3\text{Ru}_2\text{O}_7$, $\text{Sr}_3\text{Mn}_2\text{O}_7$ is an antiferromagnetic insulator due to exchange splitting of the t_{2g} orbitals [2]. Nevertheless, doping with Mn should substantially renormalize the SOC required for the appearance of the Mott state. Our results from neutron diffraction and magnetic susceptibility show a suppression of the magnetic ordering temperature without a substantial increase in the ordered moment. While all measured samples remained insulating, the inflection in the resistivity at T_N is rapidly suppressed upon Mn substitution. Intriguingly, the monoclinic lattice distortion observed in $\text{Sr}_3\text{Ir}_2\text{O}_7$ is also substantially reduced. These results indicate that Mn-doping represents an intriguing new pathway for the suppression of the Mott state, while also allowing for an investigation of the interplay between nuclear structure and electronic properties in the RP iridates.

This work was supported under ARO Award W911NF-16-1-0361.

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P10: Examining the Impact of Dispersity on Polymeric Materials

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We recently reported a versatile and scalable approach to access a library of monodisperse oligomers from a wide range of monomer families [1]. Such monodisperse materials have allowed mixtures with tailored dispersity to be prepared and their properties examined with unprecedented accuracy. In one study, oligo(3-hexylthiophene) was separated into a library of discrete species, each with distinct optoelectronic properties. Upon mixing these discrete species, a series of artificially polydisperse samples having similar average number of molecular weight were found to give remarkably different fluorescence (Figure 1).

This work is supported by MRSEC program of the National Science Foundation (DMR 1121053) and The Dow Chemical Company through the Dow Materials Institute at UCSB. B.O. thanks the Feodor Lynen Research Fellowship from Humboldt Foundation. E.G. thanks the fellowship from Japan Society for the Promotion of Science.

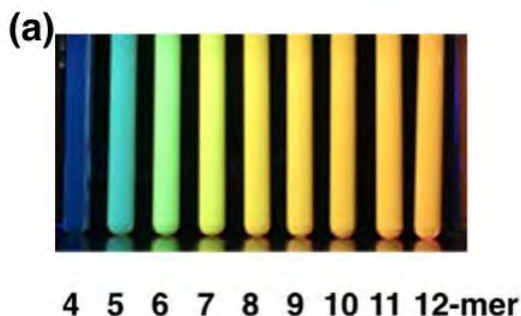


Figure 1. (a) Discrete oligo(3-hexylthiophene) samples (4-mer to 12-mer), isolated from one synthesis-purification step.

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P11: Fantastic Magnets and Where to Find Them

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Alternate cycles of isothermal magnetization and adiabatic demagnetization applied to a magnetocaloric material can drive refrigeration in very much the same manner as cycles of gas compression and expansion. The material property of interest in finding candidate magnetocaloric materials is their gravimetric entropy change upon application of a magnetic field under isothermal conditions. There is, however, no general method of screening materials for such an entropy change without actually carrying out the relevant, time- and effort-intensive magnetic measurements. Here, we show a simple computational proxy based on carrying out non-magnetic and magnetic density functional theory (DFT) calculations on magnetic materials.

This proxy, which we refer to as the magnetic deformation Σ_M , is a measure of how much the unit cell deforms when comparing relaxed unit cells of a compound with and without the inclusion of spin polarization. Σ_M appears to correlate very well with

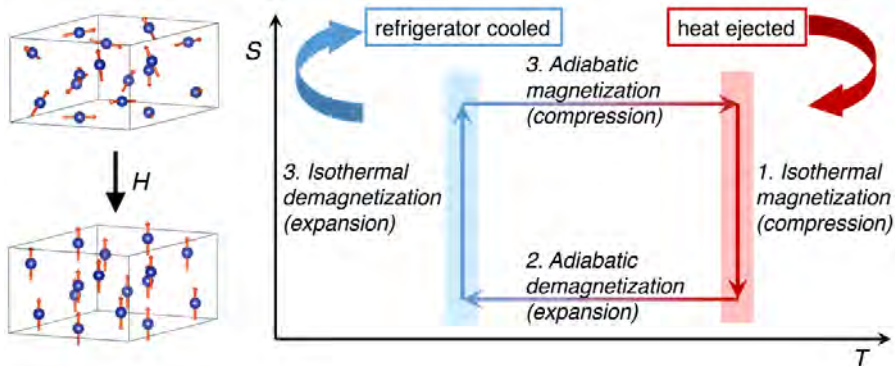


Illustration of the Carnot cycle for magnetic refrigeration, which is analogous to the conventional vapor-compression cycle.

experimentally measured magnetic entropy change values obtained from the literature and our own measurements, and we have used this proxy to screen 134 ferromagnetic compounds for which the magnetic entropy has not yet been reported, identifying 30 compounds as being promising for further study. Here, we show new magnetocaloric measurements for several of these candidate materials, which are promising for magnetocaloric applications.

The research has in part been supported by the National Science Foundation through DMR-1121053.

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P12: Fe,Ni,N-Containing Mesoporous Carbon Materials as Low-Overpotential Bifunctional Oxygen Reduction and Oxygen Evolution Electrocatalysts

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Rechargeable metal-air batteries are a promising energy storage technology, due to their high energy densities, which could enable significant decreases in the mass of consumer electronics and increases in the range of electric vehicles [1]. However, no single catalyst material has been identified which has sufficient activity for both the oxygen reduction reaction (ORR), used during battery discharge, and the oxygen evolution reaction (OER), used during charging. Presently, mixtures of Pt, Ir, and their oxides are used, where the Pt catalyzes the ORR and the Ir catalyzes the OER [2], but the use of precious metals renders these catalyst combinations unsuitable on large scales. We report iron-, nickel-, and nitrogen-containing mesoporous carbon electrocatalysts that exhibit high activities for both the ORR and OER, making them suitable for use in metal-air batteries. These catalysts were synthesized by pyrolyzing a widely-used inexpensive organic precursor within mesopores of silica templates, with a presence of metal-containing salts. The resulting materials exhibit high surface areas (~800 m²/g) and relatively high surface heteroatom contents, which enable their promising catalytic activities. Differences in cycling stabilities at high- and low-potentials indicate that the OER and ORR active sites are distinct, and comparison of polarization curves of materials with and without N indicates that N-containing sites are crucial to ORR activity, but not to OER activity. With optimization of surface N functionalities, Fe,Ni,N-containing mesoporous carbons exhibit ORR activities comparable to Pt-based catalysts. Separately, the initial Fe:Ni precursor ratio and overall metal contents were optimized to increase the OER activities of the resultant materials. Specifically, it was found that a synergistic effect of combining metal species was greatest with a ratio of 1Fe:3Ni, and that this material exceeded Ir-based OER catalysts. The materials prepared with combined optimization of N functionalities and metal contents exhibit smaller combined overpotential requirements than many previously proposed Pt- and Ir-free metal-air battery catalysts [3]. High activities for both reactions and low precursor costs make these Fe,Ni,N-containing carbon materials promising metal-air battery catalysts. Current efforts focus on providing greater certainty regarding the nature of the metal-containing OER active site and increasing the stability of the catalysts during repeated potential cycling.

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P13: Hierarchical Structure and Structural Transitions of a Conjugated Polyelectrolyte in Aqueous Solution

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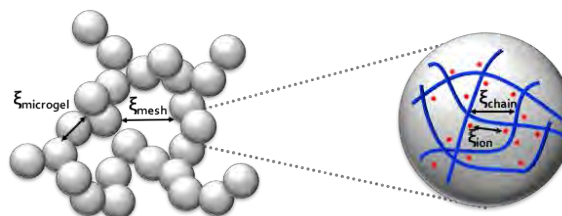
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The microscopic network structure and structural transitions of a conjugated polyelectrolyte (Poly[2,6-(4,4-bis-potassium butanysulfonate-4H-cyclopenta-[2,1-b;3,4-b']-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)], CPE-K) were explored with X-ray and neutron scattering to highlight a novel, hierarchical structure formed upon gelation of CPE-K in water in the semi-dilute regime. CPE-K forms an entangled polymer mesh, where polymer chains are tied together by ionic crosslinks, comprising microgel clusters that percolate to form a macroscopic network. Melting of the gel structure with increasing temperature occurs through the dissolution of ionic crosslinks where ions gain mobility to move towards the exterior of microgel clusters inhibiting network percolation through electrostatic repulsion. Further, CPE-K lacks π - π stacking interactions, yielding conductive matrices that rely exclusively on intra-chain charge transfer.



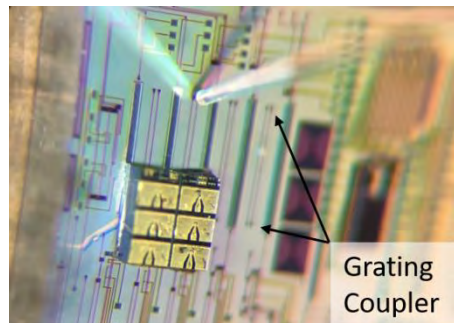
Proposed hierarchical structure for hydrogels formed by conjugated polyelectrolytes in semi-dilute aqueous solutions.

P14: InP Based Lasers and Photodetectors Integrated on Si for Next Generation Data Transmission

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Current trends in information sharing require higher bandwidth for communication over both short and long distances. While fiber optics have been used extensively in long haul communication, silicon photonics integrated circuits (PICs) are a promising new technology for both short and long range communication owing to the advantages of low size, weight and power (SWaP) compared to bulk optics [1]. Additionally, large scale fabrication of Si PICs may take advantage of existing 300 mm CMOS manufacturing infrastructure for electronics. However, silicon's indirect band gap necessitates integration of direct band gap materials for the active components of these PICs. Here we report on two methods for integrating III-V optoelectronics for light generation and detection onto silicon and silicon PICs.



InGaAs uni-traveling-carrier photodiode bonded to a silicon photonics platform.

The simplest approach to integration of III-V devices on silicon photonics is through bonding [2]. Shown in Fig. 1 is a InGaAs uni-traveling-carrier photodiode bonded to a silicon photonics (SiPh) chip. Design of a high-speed photodiode, with large saturation limit will be shown for integration of a SiPh optical beam forming network for high speed communication. Another approach for integration to reduce SWaP is direct epitaxial growth of III-V compounds on Si [3]. Here we report on the growth of InP on patterned Si (001) substrates by selective area metal-organic chemical vapor deposition (MOCVD). Growth of densely packed InP nanowires has been achieved with highly uniform facet morphology. These nanowires were then coalesced into a single thin film and planarization was achieved without any additional polishing steps. Quantum well regions grown on Si using this method show photoluminescence at the relevant telecom wavelength of 1550 nm.

The research reported in the paper has in part been supported by the American Institute for Manufacturing of Photonics, Johns Hopkins University Applied Physics Lab, and the National Science Foundation.

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P15: *In Situ* Structural Measurements of Soft Materials in Arbitrary Deformation Fields

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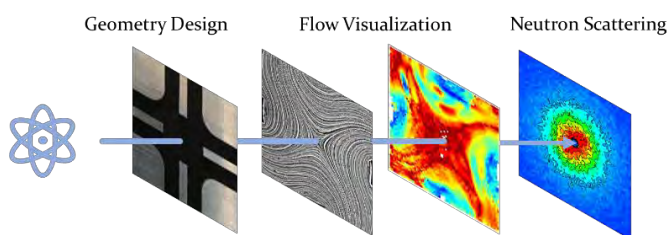
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Industrial processing of soft materials induces a wide range of flow histories that change the material's microstructure and the properties of the final product. Current means for measuring flow induced microstructural changes have focused on purely shearing or extensional deformation types, but these highly idealized deformation types fail to probe the behavior of soft materials under realistic processing conditions [1]. We present a new millifluidic four roll mill (mFoRM) for *in situ* small-angle neutron scattering (SANS) measurements of complex fluids in mixed flows. The mFoRM sample environment is capable of interrogating microstructural changes of soft materials in arbitrary near-2D deformation fields.

A characterization of cellulosic nanocrystals (CNC), a rigid, rod-like material, in solution was employed to demonstrate the capabilities of this platform. A previously designed fluidic four-roll mill was geometrically parameterized and optimized using computational fluid dynamics [2]. After fabrication of the optimized device, particle tracking velocimetry enabled the experimental verification of the simulated flow field. With an operational map of flow conditions to deformation field, SANS measurements were made on the sample as it encountered deformation types between shear and extensional. This mFoRM-SANS study yielded the direction of preferred orientation and degree of orientation of the CNC as a function of deformation type and rate. The results are compared to a model of dilute rods in arbitrary flow [3].



Pictorial outline of mFoRM-SANS studies. The parameterized mFoRM geometry is optimized for a particular soft material. Flow field visualization enables the operational mapping of the deformation field the fluid experiences. Small-angle neutron scattering probes structural changes in the material under arbitrary deformation histories at 1-100 nanometer length scales.

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P16: Insulator-Metal Transitions in Complex Palladium Oxides

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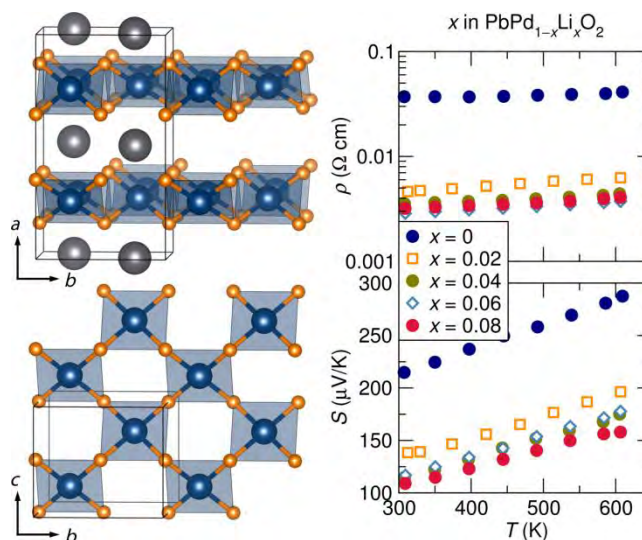
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Complex palladium oxides are rare examples of oxides that can be easily hole-doped to drive insulator to metal transitions. By examining these compositionally driven transitions in various complex palladium oxides, we can both understand their mechanisms as well as study the change in functional properties for applications such as thermoelectrics. We have found Li substitution in diamagnetic PbPdO_2 leads to electronic properties nearly identical to state of the art oxide thermoelectrics which are believed to derive their properties from degenerate magnetic states [1]. In $\text{A}_{1-x}\text{Na}_x\text{Pd}_3\text{O}_4$ ($A = \text{Ca}, \text{Sr}$) we observe the influence of local disorder on the onset of the percolative insulator-metal transition using local structural probes. While the Ca compound is driven metallic with Na substitution, increased local disorder in the Sr material acts as a barrier to bulk metallicity.



Li-substituted PbPdO_2 (structure on left) shows thermoelectric properties on par with other high performing oxide thermoelectrics.

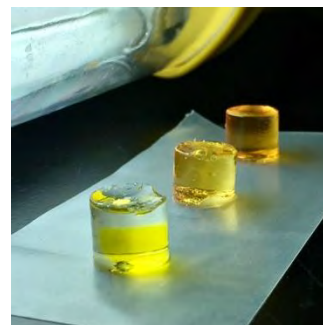
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P17: Light as a Tool to Reversibly Activate Cross-link Exchange in Vitrimers**A. Abrams,^a J. Self,^a C. Sample,^b C.M. Bates^b**^aDepartment of Chemistry and Biochemistry, and ^bDepartment of Materials, University of California, Santa Barbara, CA 93106

A new class of dynamic polymer networks coined “vitrimers” have the unique ability to relax stress when heated, while maintaining a constant cross-link density [1]. We seek to reversibly activate this trait using light. Thus, we have embedded photoacid molecules [2] within ester-containing polymer networks, which are shown to switch upon irradiation using visible-light (see figure). Switching of photoacid molecules within these networks requires an optimal chemical and structural design, including an appropriate solvent swelled into the gel. Further rheological characterization of these gels is necessary to demonstrate this photoacid is a suitable catalyst for cross-link exchange reactions.



Photoacid switching within vitrimer gels after irradiating for one minute.

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P18: Lights, Camera, Action: Photoswitches and Photopolymerizations Shot in Real Time with Nuclear Magnetic Resonance Spectroscopy

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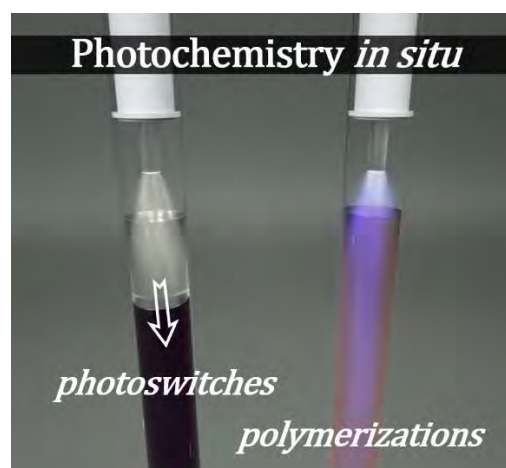
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[†]Equal contribution to this work

A simple, inexpensive and modular method to directly illuminate nuclear magnetic resonance (NMR) samples for *in situ* analysis of photochemical transformations is presented. The versatility of this technique is demonstrated by analyzing the light induced propagating front for small molecule photoswitches and the kinetics of photo-controlled living radical polymerizations. *In situ* measurements allow oxygen sensitive and rapid photoevents to be studied in detail. This led to reliable determination of photoswitching quantum yield for Donor-Acceptor-Stenhouse-Adduct (DASA) and diarylethene (DAE) photochromes. Additionally, photoinduced electron transfer-reversible addition-fragmentation chain transfer (PET-RAFT) and photoinduced atom transfer radical polymerization (photoATRP) for three monomer classes were systematically investigated to reveal a direct relationship between propagation rate and irradiation intensity. Moreover, the conditions identified through this NMR analysis procedure are shown to translate to analogous benchtop experiments and provide insight into the nature of the photoreactive species.

The research reported herein has in part been supported by the MRSEC program of the National Science Foundation (DMR 1121053), The Dow Chemical Company through the Dow Materials Institute at UCSB and the Institute for Collaborative Biotechnologies through grant W911NF-09-0001 from the U.S. Army Research Office.



Photoswitches and photopolymerizations shot in real time with nuclear magnetic resonance spectroscopy, using a simple and modular optical fiber-LED setup. The technique grants access to isomerization quantum yields for reverse photochromes and temporal monitoring for photoinduced polymerizations.

P19: Local Structure Evolution and Corresponding Charge Storage Mechanisms in Transition Metal Sulfides for Lithium Batteries

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In battery research, there is a perpetual drive for materials to enable higher energy density devices. Commercial batteries perform well and reliably, and employ materials that store charge by a mechanism called intercalation. However, materials that store charge by this method are limited to < 1 mole of Li per formula unit of a layered transition metal (TM) oxide host. To achieve higher capacities (and thus energy densities), materials that store charge by alternative mechanisms are of interest. We describe here a study of materials that store charge by a conversion mechanism, in which vast chemical and structural changes enable storage of 2 or more moles of Li per formula unit [1]. A variety of cation, anion, and structures can in theory store charge by this method, though many fall short of theoretical performance and exhibit rapid capacity fade with cycling [1]. Select TM sulfides that store charge by conversion have shown relatively promising performance [2]. To better understand the mechanism of charge storage in select TM sulfide systems, we have employed *operando* total X-ray scattering and *ex-situ* X-ray absorption methods to describe the local structure evolution. A collaboration with first principles researchers provides access to a library of structures that we find are descriptive of the local structure motifs that evolve with cycling. From a comparison of several systems for conversion-based energy storage, we propose rules for identifying relatively promising candidates [3].

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P20: Main-Group Halide Photovoltaics Derived from Perovskite

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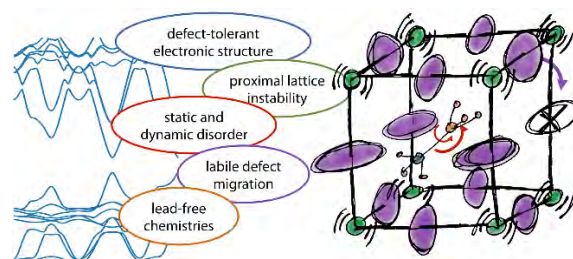
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Inorganic and hybrid organic–inorganic main-group halides that adopt the perovskite structure have attracted immense attention of late for their excellent performance in photovoltaic applications, ease of preparation, and abundant constituent elements, but the origins of their remarkable properties are a matter of debate [1]. Here, we address two unusual aspects of these materials which have significant implications for functionality. First, the size, shape, and polarity of the molecular cations are shown to have a profound effect on the temperature evolution of structure and dynamics in the lead iodides [2]. In contrast to the well-studied $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ exhibits an unusual reentrant pseudosymmetry on cooling which is reflected in the optical properties, as well as persistent molecular motion below 100 K which indicates a markedly different molecule–cage interaction in the two compounds. Second, X-ray scattering studies reveal local, temperature-activated off-centering of the group 14 cations within their coordination octahedra across the materials class [3]. Ab initio calculations, optical measurements, and analogies to existing theory implicate the lone pair electrons as the origin of this phenomenon, which we propose leads to enhanced defect screening that aids charge transport, reduced thermal conductivity, and unusual temperature-dependence of the electronic bandgap.



Disorder of the molecular cations in main-group halide perovskites results in complex evolution of structure and dynamics with temperature and composition. Additionally, the unusual crystal chemistry of the metal–halogen sublattice leads to a proximal lattice instability that affects electronic, thermal, and dielectric properties.

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under award number DE-SC-0012541.

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P21: Metal-Directed Self Assembly of Bioinspired Amphiphiles

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Nature has created a vast array of responsive polymeric architectures for structural and functional applications. Dynamic structures are critical for the complex functions of natural polymers (e.g., ion transport channels), and therefore there has been significant strides towards controlling the assembly of synthetic architectures. Currently these efforts are limited to a few chemical strategies including changes in pH, temperature, and oxidation state. Metal-ion interactions, which are critical to the structure and function of natural proteins, are currently underutilized for modulating the morphology of soft materials. We are developing a new class of nanomaterials using peptide-polymer amphiphiles that have different self-assembled structures directed by the metal coordination. These amphiphiles self-assemble in an aqueous buffer and can be transformed to multiple different morphologies with different metals ions as indicated by characterization with dynamic light scattering and transmission electron microscopy. Although the coordination environment is on the molecular scale, these differences dictate the morphologies of nanometer to micron scale assembled materials. These smart materials open the door for developing a new class of materials with applications including therapeutics that respond to complex biological environments, sensors for metal pollutants, and self-assembled electronic materials.



Figure 1 – schematic of metal-directed self-assembly.

P22: Metal-Free, Surface-Initiated Atom Transfer Radical Polymerization on the Bench Top

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Surface-initiated atom transfer radical polymerizations (SI-ATRP) are a powerful and widely utilized approach for the preparation of robust and functional polymer surfaces. Our group recently reported a light-mediated SI-ATRP process using an Iridium-based photoredox catalyst to spatially and temporally control polymer brush synthesis from uniformly functionalized initiating layers [1]. The development of an operationally simple, metal-free surface-initiated atom transfer polymerization (SI-ATRP) is reported. The facile nature of this process enables fabrication of well-defined polymer brushes from surfaces using a novel “bench top” set-up that can be easily scaled to 4-inch wafers. This approach circumvents the requirement of stringent air-free environments (i.e. glovebox), and mediation by visible light, allows for manipulation of brush thicknesses as well as spatial control on the nanoscale. 3-dimensional patterns can be achieved in a single step, allowing access to brush architectures for both experts and non-experts.

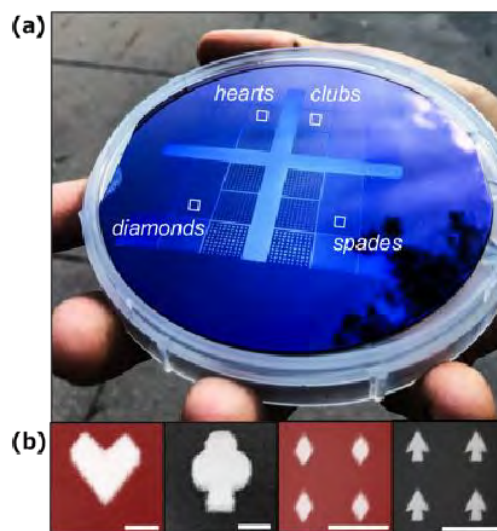


Figure 1. (a) Photograph of patterning of a 4-inch wafer in a single step using a handheld lamp and photomask. (b) Optical micrographs of arbitrary features. Scale bars are 200 μm

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P23: Mimicking Mussel Adhesives with Peptide Glue: Relating Adhesive Protein Structure to Function

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The development of glues that adhere to wet surfaces is important for medical, dental, and marine applications. However, glues that are effective in dry conditions often fail in aqueous conditions, especially in salt solutions or when the surfaces are contaminated, for example by a biofilm. Nevertheless, many marine organisms adhere to surfaces under water. The marine mussel attaches itself to rocks in the ocean by secreting proteins which adhere to fouled mineral surfaces via chemical and physical bonds. To study these interactions, a peptide glue was synthesized to mimic a common type of mussel adhesive protein (MFP-3). The adhesion energies between the peptide and hydrophobic (CH₃-SAM) and hydrophilic (OH-SAM, mica) surfaces were measured experimentally using a surface forces apparatus (SFA) and computed from molecular dynamics simulations. Changing surface hydrophobicity resulted in different peptide-surface molecular geometries, and suggested a synergistic and adaptive adhesion mechanism based on adjacent hydrophobic and hydrophilic residues. Understanding the dependence of peptide adhesion on peptide primary structure and interaction geometry will allow the design of adhesives for use in aqueous environments.

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P24: N-type Conductivity in Ga_2O_3

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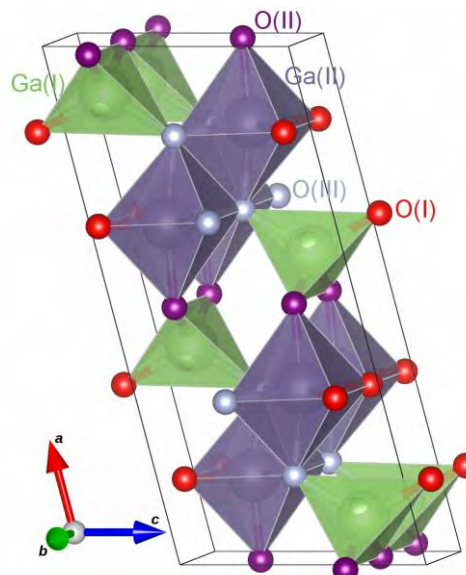
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Gallium oxide ($\beta\text{-Ga}_2\text{O}_3$) is a promising material for high-power electronic devices, combining excellent material properties and ease of mass production. It is a wide-gap semiconductor with a monoclinic crystal structure, and a band gap of 4.8 eV. Its high carrier mobility and large band gap have attracted a lot of attention for use in high power electronics and transparent conducting applications.

These applications require the presence of a large concentration of free electrons. Based on advanced first-principles calculations using hybrid functionals, we will discuss different approaches to obtain such a large concentration of free carriers. We previously found that doping with Si, Ge, or Sn on Ga sites, or Cl and F on O sites leads to shallow donors, but that Ga vacancies can each compensate 3 electrons, so that their presence compensates the n-type carriers. We now also considered non-traditional doping routes to achieve n-type conductivity in Ga_2O_3 . In particular we considered doping with the transition metals Mo, W, Nb, and Re. These transition metals are generally deep donors. The main exception is Nb, which is a shallow donor when it substitutes on a tetrahedral site, and has a small enough ionization energy to enable n-type conductivity on the octahedral site. Niobium also has the lowest formation energy among the considered transition metals.

It is also important that the carriers are mobile, but an understanding of the transport properties of Ga_2O_3 is still lacking. We will address this by analyzing the calculated electron scattering rates due to ionized impurities and polar longitudinal-optical (LO) phonon at room temperature. We find that the intrinsic anisotropy in the mobility is small, despite the low-symmetry monoclinic structure of Ga_2O_3 . For carrier densities in the range of 10^{17} - 10^{19} cm^{-3} , we find that the mobility is dominated by LO phonon scattering. We explain the strong suppression of mobility observed in experiments at higher carrier as a consequence of electrical compensation by gallium vacancies, which significantly affects the mobility.

The studies presented here were supported by the MRL IRG-2, the ARO, and the ONR EXEDE MURI.



Conventional unit cell of Ga_2O_3 , where the various atoms are labeled according to their symmetry.

P25: NV Center Ensemble Magnetometry for Biological Applications**C. A. McLellan,^a T. Eichhorn,^a D. D. Awschalom,^b A. C. B. Jayich^a**^aDepartment of Physics,

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The nitrogen-vacancy (NV) center is a point defect in diamond which is extremely sensitive to magnetic fields. Because of its combined optical addressability, ambient operating capability, and the biocompatibility of diamond, NV center ensembles are a highly promising platform for wide-field imaging of magnetic signals in biology. An outstanding challenge towards realizing an NV center based bio-magnetometer is increasing the NV center ensemble's sensitivity. To address this challenge, we have developed a technique that produces large ensembles of highly coherent NV centers. We combine PECVD grown diamond which has a nitrogen doped layer 500 nm thick with high dosage electron irradiation. This technique has produced NV ensembles with a magnetic sensitivity as low as 3 nT/ $\sqrt{\text{Hz}}$. We are working towards quantifying the nitrogen and NV center concentration in our diamond, and hence the sensitivity, via double electron-electron resonance measurements. I will present our initial results using these diamonds as a bio-magnetometer.

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P26: Revealing the Surface State Modification Effect on Strength Distribution of Au Nanowires

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Numerous and successive studies have surged on ultra-high strength materials ever since the observation of size dependent strength to understand the unique mechanical behavior [1, 2]. However, unlike in bulk materials which often exhibit deterministic strengths, the data for nanostructures show considerable scatter. Recent works from temperature controlled tensile tests on defect free nanowires suggest that the strength of these nanowires is controlled by surface atom activity which is naturally a probabilistic process at finite temperature resulting in intrinsic stochasticity [1-4].

In this work, we further investigate the surface mediated dislocation nucleation in Au nanowires of which the surface has been coated by aluminum oxide grown by atomic layer deposition. The yield strengths show temperature dependence and a large scatter in room temperature tests. The coated wires showed a slight increase in yield strength and less scatter compared to the uncoated wires. In addition, the first success on in-situ nanomechanical test on one of the nanowire at synchrotron beamline is included in the results. The coherent X-ray diffraction using nanofocused beams technique has been introduced to reveal the internal strain state of nanostructure and is expected to understand the role of the surface layer to the overall strength of the nanowire [5].

This research was supported by the NSF Career Award (DMR-1056293) and A*MIDEX Grant (ANR-11-IDEX-0001-02).

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P27: Role of Backbone Chemistry and Monomer Sequence in Amphiphilic Oligopeptide- and Oligopeptoid-functionalized Block Copolymers for Marine Antifouling Coatings

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The design rules elucidated in this work suggest that antifouling coatings bearing pendant peptoid side chains perform better overall in marine fouling tests than those with peptide side chains, with extremely low attachment of *N. incerta* and high removal of *U. linza*. This difference in performance is likely due to the lack of a hydrogen bond donor in the peptoid backbone. Furthermore, we show that the bulk polymer material of these hierarchical coatings (based on PEO or PDMS) plays a key role in determining both surface presentation and fouling release performance. We demonstrate these trends utilizing a modular coating based on a triblock copolymer consisting of polystyrene and a vinyl-containing midblock, to which sequence-defined pendant oligomers (peptides or peptoids with sequences of oligo-PEO and fluoroalkyl groups) are attached via thiol-ene “click” chemistry (following [1] and [2]). Surface presentation was analyzed with X-ray photoelectron spectroscopy and captive bubble water contact angle, and antifouling performance was evaluated with attachment and removal bioassays of the marine macroalga *U. linza* and diatom *N. incerta*.

The research reported has in part been supported by the Office of Naval Research under a Presidential Early Career Award in Science and Engineering (R.S.).

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Subtle differences in side-chain chemistry resulted in significant differences in antifouling performance.

P28: Scalable Colorimetric Sensor for Selective and Sensitive Amine Detection

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The use of stimuli responsive materials as smart sensors has rapidly expanded to a broad range of applications including drug delivery, biosensors, coatings, and textiles. Although simple and portable sensing techniques are highly desirable, easy-to-use systems often result in a loss of sensitivity and selectivity. This work presents the utility of Meldrum's activated furan for the creation of colorimetric amine sensors that are both highly selective and affordable. In addition, the use of these sensors for various applications including food spoilage detection, thin layer chromatography, and solid state synthesis will be demonstrated.

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P29: Self-Assembly and Crystallization of P₃EHT Containing Block Copolymers

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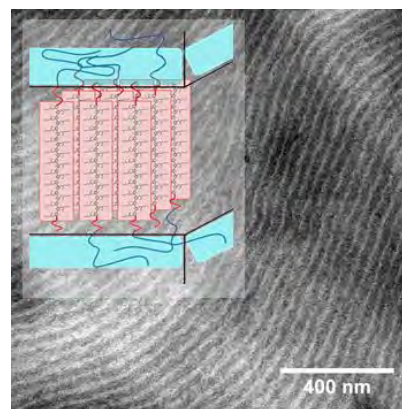
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Conjugated polymers are of considerable interest for organic electronic devices, and the crystallization of conjugated polymers is highly coupled to their charge transport properties. Here, block copolymers are leveraged as a controlled platform to study the impact of confinement on conjugated polymer crystallization. In particular, the polymer P₃EHT is leveraged as a model system in these diblock architectures because the depressed melting transition relative to the widely-studied P₃HT enables both robust microphase separation of the resulting diblocks and detailed control over the crystallization processes. A series of block copolymers with rubbery PMA and glassy PS second blocks were synthesized to investigate the impact of chain tethering on the resulting crystallization. All diblocks robustly self-assemble in the melt, forming both lamellar and (minority P₃EHT) cylindrical morphologies. The resulting crystalline P₃EHT successfully confined within P₃EHT-*b*-PMA microdomains illustrates the importance of careful design strategy to balance the driving force for crystallization (which can result in crystallization dominated self-assembly) with large segregation strengths (which can impede block copolymer ordering kinetics). While P₃EHT successfully crystallizes with a rubbery poly(methyl acrylate) block, crystallization is inhibited when confined by a glassy PS block. X-ray scattering of shear-aligned crystallized P₃EHT-*b*-PMA reveals that microdomains induce an orientation of chains perpendicular to the domain interfaces. Furthermore, P₃EHT-*b*-PMA samples exhibit considerable expansion of domains upon crystallization, emphasizing that P₃EHT prefers to form extended-chain crystals in confinement. The inhibited crystallization in P₃EHT-*b*-PS is attributed to the inability of glassy PS domains to accommodate either the extended chain P₃EHT crystals or local densification of chains at the interface [1]. This work emphasizes the unique constraints that the drive for extended-chain crystallization places on self-assembly, and the importance of considering these interactions when designing such hierarchical architectures.



Block copolymers containing the conjugated polymer P₃EHT self-assemble into microphase separated domains in the melt; microdomains morphology and block identity distinctly template and control crystallization.

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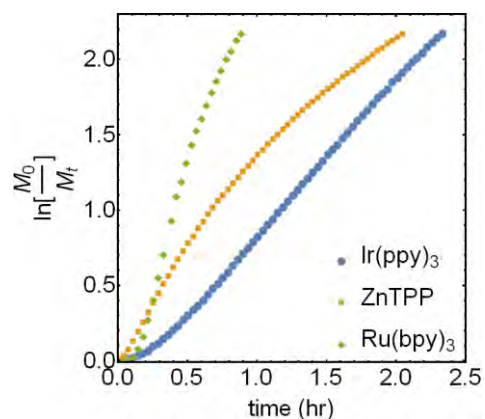
P30: Shedding Light on State of the Art Photo-mediated Controlled Polymerizations

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The use of light to initiate and mediate controlled radical polymerizations has been a growing area of interest in the polymer community given its simple access to spatial and temporal control. Currently, photo-mediated control has been demonstrated in various systems, with the most commonly utilized methods including transition-metal [1] and Cu [2,3] catalyzed atom transfer radical polymerization (ATRP), and photoinduced electron transfer-reversible addition-fragmentation chain transfer (PET-RAFT) [4]. Despite this rapid growth in the field, little attention has been given to the effects of light intensity/wavelength and catalyst absorption cross-section on polymerization efficiency. The use of traditional aliquoting, where small volumes of sample are extracted from an active reaction, to monitor kinetics has become the main barrier to these systematic studies.

Since polymerizations can be quite sensitive to both volume changes and oxygen, aliquots can have deleterious effects on polymerization kinetics, often manifested by a small number of data points for a given reaction. Using a newly developed method for *in situ* analysis of photopolymerizations *via* fiber-coupled nuclear magnetic resonance (NMR) spectroscopy, a single sample can be measured throughout the entire polymerization process, thereby giving access to rich kinetic data. Additionally, the use of modular and controllable light emitting diodes allows for precise changes in wavelength as well as intensity. This presentation shows the impact of light intensity and catalyst absorption on the rate of polymerization, as well as a study of temporal control for several polymerization systems.



Kinetics of methyl acrylate polymerization by PET-RAFT with various photocatalysts, measured using fiber-coupled NMR.

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P31: Synergistic Effects Between Functional Cations and Heavy Metal Halide Networks in Tetrathiafulvalene Pb/Bi Iodide Hybrid Materials

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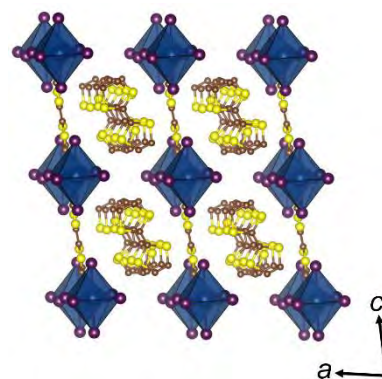
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Hybrid organic–inorganic materials offer a unique opportunity to utilize the combined functionalities of two distinct chemistries. Here, we present our work on exploring new optoelectronic hybrid materials, where understanding how structure and the nature of functional organics can predict behavior and performance. Specifically, we have explored the effect of a radical organic cation (tetrathiafulvalene) [1] incorporation with already optoelectronically active inorganic matrices (lead-iodine, bismuth-iodine).

We present successful isolation and complete analysis surrounding two new radical bismuth iodides, (TTF)BiI₄ and (TTF)₄BiI₆, [2] and compare them to the previously isolated compound (TTF)Pb₂I₅, which showed a synergistic back-charge transfer between the inorganic and organic network [3]. The compound (TTF)₄BiI₆, crystallizes in a previously unseen structure, and has mixed-valence stacks of TTF and TTF^{•+} and discrete molecules of TTF^{•+} separated by discrete [BiI₆]^{−3} anions. These compounds are found to be narrow gap semiconductors, governed primarily by the organic component.



Full Crystal structure of (TTF)₄BiI₆ looking down the b-axis, emphasizing the BiI₆^{−3} octahedra and eclipsed nature of the mixed-valence TTF stack

References:

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P32: Thermoelectric Properties of Half-Heusler Materials: Role of Microstructure and Disorder

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Thermoelectric materials reduce energy loss by converting waste heat into electricity. Half-Heusler materials, such as TiNiSn and NbCoSn, are favored for thermoelectric applications due to their large Seebeck coefficients, high temperature stability, and composition of relatively Earth-abundant elements. These half-Heusler materials are subject to various forms of structural disorder as a function of materials processing, which impacts the resultant thermoelectric properties. In this work, we evaluate the relationship between thermoelectric performance and preparation by considering microstructure and disorder in various systems.

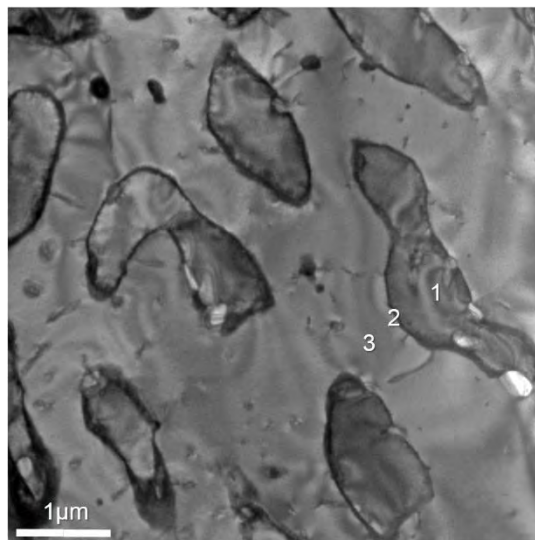
First, we report on biphasic NbCoSn-NbCo₂Sn, noting that not only does the addition of a second phase improve thermoelectric performance, but that an annealing processing step impacts Nb-Co site occupancies and thermoelectric performance

[1]. Next, we share a report evaluating the impact of annealing on the existence of Ni-interstitials in TiNiSn [2]. Finally, we consider the thermoelectric performance of the solid solution between NbCoSn and TiNiSn, utilizing our understanding of these systems from the previous reports [3]. Comparing these studies, we realize that structurally ordered materials are not necessarily the best thermoelectric materials. Understanding the relationship between order and performance is critical to the development of future thermoelectric materials.

The research reported has been supported by the National Science Foundation.

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TEM micrograph highlighting the interface formed between half-Heusler NbCoSn (matrix) and Heusler NbCo₂Sn (particulates).

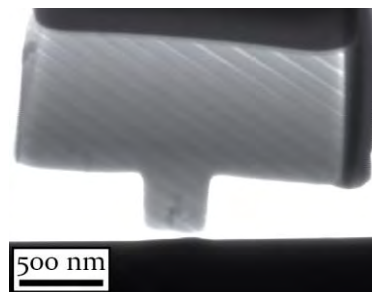
P33: Toughening Mechanisms in the $\text{ZrO}_2\text{-YO}_{1.5}\text{-TaO}_{2.5}$ Ternary System

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Although the $\text{ZrO}_2\text{-YO}_{1.5}\text{-TaO}_{2.5}$ ternary system contains several single phases exhibiting one or more properties that are useful in thermal barrier coating applications, e.g. low thermal conductivity [1], sintering resistance, considerable toughness [2], and reactivity with molten silicates, none of the single phases alone displays an appropriate balance of the requisite attributes. The potential to blend the material response of the various phases together to achieve exceptional combinations of properties motivates investigation into the behavior of multiphase compositions. This study explores the trends in toughness as a function of phase content in the three-phase field containing the tetragonal zirconia solid solution, fluorite, and yttrium tantalate and connects the observed response to the microstructural aspects of fracture. Indentation results suggest that the high toughness of the tetragonal phase diminishes rapidly with the addition of either second phase. Analysis of fracture surfaces and indentation cracks indicates that the mode of fracture and crack propagation pathways varies between each phase and play a critical role in understanding the active toughening mechanisms. Ongoing TEM microscopy and STEM *in-situ* pillar compression tests aim to verify ferroelastic switching as a toughening mechanism in the tetragonal zirconia phase as well as domain boundary motion as a toughening mechanism in twinned monoclinic yttrium tantalate.



Twinned monoclinic tantalate (YTaO_4) pillar being compressed *in-situ*. Image taken in bright-field STEM mode.

The research reported in the paper has in part been funded by the Honeywell-UCSB Thermal Barrier Coating Alliance under the Contract PO350152800E.

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P34: Transport in Complex Oxides: Understanding Mobility from First Principles

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Complex oxides have emerged as potential candidates for novel electronic applications. Adequate electron mobility is a critical requirement for good device performance. First-principles calculations can provide essential information about microscopic scattering mechanisms impacting and limiting electron transport in these materials. We present our first-principles studies of electron-electron, longitudinal optical (LO) phonon, and ionized impurity scattering mechanisms in a number of key complex oxides: strontium titanate (SrTiO₃), barium stannate (BaSnO₃), and tungsten oxide (WO₃).

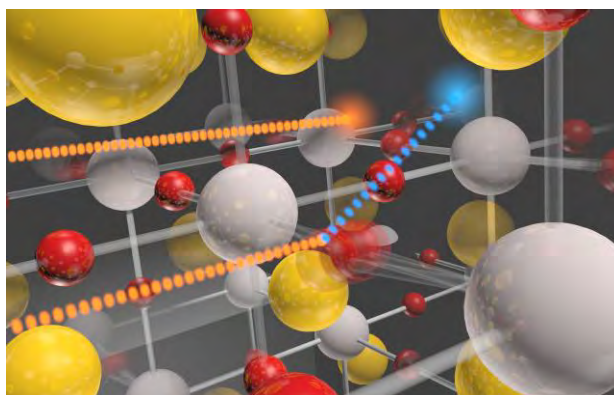


Illustration of electron-phonon scattering in a complex oxide.

Transport measurements in SrTiO₃ show a regime in which resistivity follows a power law in temperature ($\rho \propto T^2$). By analogy to a similar phenomenon observed in some metals at low temperature, this has often been attributed to electron-electron (Baber) scattering. We show that Baber scattering results in a T^2 power law only under several crucial assumptions, which do not hold for SrTiO₃. Our explicit numerical calculations show that the temperature dependence in SrTiO₃ deviates significantly from T^2 . We conclude that an observation of $\rho \propto T^2$ is not sufficient evidence for electron-electron scattering.

The room-temperature (RT) mobility of SrTiO₃ is limited to 10 cm²V⁻¹s⁻¹. Based on our analysis, the limiting factors are strong LO phonon scattering as well as the large electronic density of states. Based on these insights, we predict BaSnO₃ and WO₃ to have a higher RT mobility compared to SrTiO₃ due to a reduction in LO-phonon scattering from a smaller DOS. Based on the accurate first-principles methodologies that we developed, we compute the RT mobility in BaSnO₃ to be ~300 cm²V⁻¹s⁻¹ and the mobility in WO₃ to be ~90 cm²V⁻¹s⁻¹. The methodologies and results of our analysis are general and can be used to understand transport in many other materials systems.

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P35: Understanding Domain Connectivity in Semiconducting Polymer Thin Films

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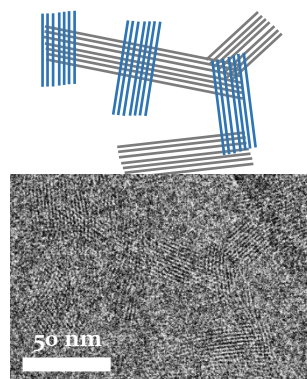
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The morphology of a semiconducting polymer thin film has a large effect on the charge transport properties. It is known that charge carriers can easily move along the conjugated backbone and in the pi-pi stacking direction. However, transport between adjacent domains is determined by the specific connectivity at the grain boundaries and is not as well understood. In the polymer PSBTBT, the first example of a semiconducting polymer exhibiting a nonparallel stacking of the backbones was observed using high resolution transmission electron microscopy (HRTEM) [1]. It was proposed that the preferential overlap between lamellae - at an angle determined by the length of the polymer repeat unit and side-chains - may provide an additional conduction pathway. Now, the same effect is observed in another successful donor polymer, PBDTTPD. The factors driving the epitaxial arrangement of the backbones are examined using several PBDTTPD derivatives with different side-chain attachments. Direct imaging of the cross-chain structures is achieved using HRTEM and the effect of these structures on film texture is examined with grazing wide-angle X-ray scattering (GIWAXS). It has been shown that heating some semicrystalline polymers above the melting temperature and slow cooling can flip the lamellar texture from face-on to edge-on [2]. Here, the presence of cross-chain structures can be correlated with the percentage change in film texture from face-on to edge-on after extended high-temperature annealing. It is proposed that the orientation of crystallites in PBDTTPD films is stabilized by the epitaxial overlap between adjacent crystalline domains. This may have important implications for the electronic transport properties of thermally processed thin films.



HRTEM image of PBDTTPD thin film showing nonparallel stacking of crystallites

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P36: Understanding Electrical Conductivity of Semiconducting Polymers Through Vapor Phase Doping

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Organic semiconductors provide a unique opportunity for developing large area, flexible electronics such as solar cells, displays, and wearable electronics. In order to better understand the performance of electronic devices, there has been significant progress in studying the structure – property relationship of organic semiconductors. The morphology of the semiconductors over large length scales can be controlled by molecular design and processing methods to achieve improved performance of organic semiconductors.

Enhancing the electrical conductivity of semiconducting polymers has been of great interest for many applications in organic electronics including electrode layers and thermoelectric devices. One method to increase the electrical conductivity of polymers is through chemical doping with dopant molecules that increase charge carrier density through charge transfer between the polymer chain and the dopants. Finding an efficient doping method is important as doping methods in thin films affect the film morphology, which is closely related to charge transfer.

In this work, we used the vapor-doping method to examine the electrical conductivity of the widely studied polymer, P3HT. Previously, doping methods such as solution and sequential doping has been explored for this system and show two phases (doped and undoped) in the resulting films. We used grazing incidence wide-angle scattering (GIWAXS) to show that upon vapor doping, a second crystalline phase appears similar to other methods. GIWAXS suggests formation of a larger number of heavily doped regions from the intensity of π stacking peaks, but the maximum measured electrical conductivity was similar. In order to better understand the impact of doping on morphology and electrical properties, we used resonant soft x-ray scattering (RSOXS) on doped films to probe amorphous and crystalline regions of the films over larger length scales. RSOXS showed that vapor doping has little effect on the connectivity between the crystalline regions explaining the lack of a significant increase in conductivity in the P3HT films. This work allows us to better understand morphological influences on chemical doping methods, which can open up new possibilities of exploring efficient doping methods.

P37: Uranium Containing Endohedral Fullerenes: Synthesis and Purification

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The first instance of encapsulation of a metallic atom by a carbon cage was reported 1991 by Smalley et al [1]. These new molecular structures, known as endohedral metallofullerenes (EMFs), have since grown in variety to include many different metals within a range of carbon cage sizes and geometries. One year after their discovery of EMFs, Smalley and coworkers found experimental evidence for the existence of Uranium containing endohedrals [2]. These unprecedented compounds may possess remarkable characteristics and properties which might be practically useful and fundamentally insightful [3]. Though their properties have been theorized and their existence observed by analytical techniques, uranium endohedrals have yet to be isolated and characterized. Poor yields coupled with complex, inefficient purification methods have been the major obstacles to obtaining appreciable amounts of these chemical species. In this work, we report our recently developed methods for optimization of synthesis and chromatographic separation of uranium endohedrals. We demonstrate the effectiveness of our methods by purification and characterization of some isolated uranium EMFs (See Figure 1). We also show the synthesis of never before reported diuranium-cluster (2 uranium atoms bonded to non-metallic atoms) endohedral fullerenes.

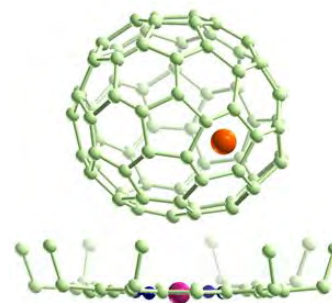


Figure 1: Crystal Structure of U@C₇₄

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